

On the mechanism of eutectic structure

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Abstract The criteria for stabilities of eutectics, solid solutions and precipitates are proposed. Based on the Thomas-Fermi-Dirac model on the boundary conditions, electron densities and chemical potentials should be equal in either side of a composite film. The optimum condition for the energy balance and the sizes of films of eutectics is given.

Keywords: Thomas-Fermi-Dirac, eutectics, internal stress, chemical potential, electron density.

The phase diagram of a eutectic structure is characterized by the equality of chemical potentials of three phases (two component phases and one composite phase). From the angle of first approximation, neither significant surface tension nor difference of surface energies should exist at the boundaries of micro-crystals. A mixture of the three phases in any size of crystallines will be stable. The sizes of crystals are insignificant for the stability of the structure. In general, however, equilibrium between two components is possible but not in the composite phase with a mean density. The composite phase is then either more, or less stable than that of the simple mechanical mixture of the separate phases. This means that there exists a large difference in chemical potentials at the interfaces of the crystals of the three phases, and the mixture of two component phases cannot coexist with the composite phase. Hence all crystals tend to grow as large as possible until the boundary energies are the least. However, to a next higher approximation there will be differences in the free energies among the three phases in a eutectic mixture. Here one has to take account of the surface energies at boundaries of the crystallines. Although their difference is small, they do affect the structure of the component phases. At the interface boundary, there are several independent factors controlling the thickness of each kind of crystallines in contact. They are as follows.

(i) In general the composite phase either stays alone or completely disappears. In the following we shall only consider the latter case, because the former is the case of simple chemical reaction.

(ii) The difference in electron densities of the crystallines of two contacting components gives rise to stresses at interface and stress energies in a relatively broad micro-centimeter scale. The energy increment is positive^[1].

(iii) A difference in the chemical potentials of electrons on two sides of the interface will create a shift of electrons from one side to the other. This will decrease the total energy. The increment is therefore negative^[2].

(iv) The increment of stress energy in (ii) and decrement of energy by electronic transference in

(iii) will reach counterbalance to a stable level. This determines the optimum sizes of the two adjacent crystals of the two components.

(v) The constituent ratio of the two components can be known from the condition of the phase diagram, namely the lever rule, but the actual thickness of the components cannot be determined. The energy balance results in the stacking-up of alternative layers of two components in definite thickness. This is exactly the pattern of the eutectic structure.

1 Phase relation of the eutectic

Figure 1 shows the free energy F against concentration of one component for a eutectic. Because the three phases are all in equilibrium, their tangents are in one line. The equations for equilibrium are as follows:

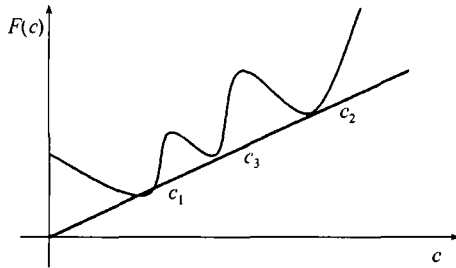


Fig. 1 Phase diagram of a eutectic, the free energy versus composition.

$$\frac{dF(c_i)}{dc_i} = \frac{F(c_i) - F(c_j)}{c_i - c_j}, \quad i, j = 1, 2, 3, \dots, \quad (1)$$

where c_i and c_j are concentrations of components. Eq. (1) shows that three phases can coexist with equal chemical potential. This means that no significant forces exist at the interfaces and micro-crystalline can exist in all possible sizes. The quantity of each specimen obeys the lever law

$$(c_i - c_j)M_i = (c_M - c_j)M_j, \quad (2)$$

where $M_i = F(c_i) - F(c_j)$, $M_j = F(c_M) - F(c_j)$ and c_M is the concentration of M component.

Actually, the difference in free energy or chemical potential, though very small, does exist as mentioned above.

2 Change in free energy at interface due to transference of electrons

The transference of electrons from one side to the other side of the interface results in a decrease in energy. We first assume that both components are metallic. This change in energy can be computed by applying the Thomad-Fermi-Dirac (TFD) model. For the other case where one component is metallic and the other is an insulator, please refer to References [1,2].

Consider plane interface here, and let the origin of the coordinate system be at the interface such that the positive direction of x axis refers to the direction from the interface to one component, and the negative one refers to that from the interface to the other component. denote by $\eta = \eta(x)$ the change in density of electrons $n(x)$ at position x , and by $V = V(x)$ the Coulomb potential. Let μ be the difference in chemical potential of an electron at the interface. One can now write down the total change in free energy ϵ per unit cross section as

$$\epsilon = \int \left[\frac{1}{2} A \eta^2 + \left(B + \frac{1}{2} eV - \mu \right) \eta \right] dx, \quad \eta = n - n_0,$$

$$\begin{aligned}
 A &\equiv \frac{\hbar^2}{3m} \left(\frac{3}{8\pi} \right)^{2/3} n_0^{-1/3} - \frac{1}{3} \left(\frac{3}{\pi} \right)^{2/3} e^2 n_0^{-2/3}, \\
 B &\equiv \frac{\hbar^2}{2m} \left(\frac{3}{8\pi} \right)^{2/3} n_0^{2/3} - \left(\frac{3}{\pi} \right)^{1/3} e^2 n_0^{1/3}, \\
 x &> 0, \mu = \mu; \quad x < 0, \mu = 0,
 \end{aligned} \tag{3}$$

where η refers to the deviation of densities from that of the ground state, \hbar is the Plank constant, m the electron mass and e the electron charge. A and B are the first and the second derivatives of total TFD energy density against electron density n respectively. The factor of 1/2 before the potential energy term takes account of the fact that each term of n appears twice in the integration.

The potential $V(x)$, together with the boundary conditions at $x = 0$, is given by

$$\begin{aligned}
 \Delta V(x) &= -4\pi\eta, \\
 x = 0, \quad V(+0) &= V(-0), \\
 \frac{dV}{dx}(+0) &= \frac{dV}{dx}(-0).
 \end{aligned} \tag{4}$$

The distribution $\eta(x)$ is determined by the variation in Eq. (3) with the aid of Eq. (4).

$$\begin{aligned}
 A\eta + B + eV - \mu &= 0, \\
 \eta &= -\frac{1}{A}(B + eV - \mu), \\
 \Delta\eta &= \frac{4\pi e^2}{A}\eta.
 \end{aligned} \tag{5}$$

The solutions of Eqs. (4) and (5) are

$$\begin{aligned}
 \eta_{\pm} &= \eta_{0\pm} e^{\mu \frac{x}{x_0}}, \\
 x_{0\pm} &= \sqrt{\frac{A_{\pm}}{4\pi e^2}}, \\
 \eta_{+0} &= \frac{1}{\sqrt{A_+}} \frac{B_- - B_+ + \mu}{\sqrt{A_+} + \sqrt{A_-}}, \quad \eta_{-0} = \frac{-1}{\sqrt{A_-}} \frac{B_- - B_+ + \mu}{\sqrt{A_+} + \sqrt{A_-}},
 \end{aligned} \tag{6}$$

where + and - denote the regions $x > 0$ and $x < 0$, respectively.

The total change in free energy per unit area can now be evaluated and given as

$$\epsilon = -\frac{1}{2} \frac{1}{\sqrt{4\pi e^2}} \frac{(B_- - B_+ + \mu)^2}{\sqrt{A_+} + \sqrt{A_-}} = -\epsilon_0, \quad (7)$$

which is small if the chemical potential and difference $(B_- - B_+)$ are small. That will be true for the eutectic structure. This requirement is critical in the following sections. We will demonstrate that eutectics can have two possible stable structures, one of which is formed by stacking alternatively the thin films of two components.

3 Increase in stress energy at the interface

In Fig. 2, A and B are two kinds of specimen of materials. There exist^[1] stresses on both sides of the interface between A and B , with opposite sign and magnitude proportional to the difference in electron densities of the two sides of the interface. The pressure inside a layer will be the superposition of pressures from both sides of interfaces.

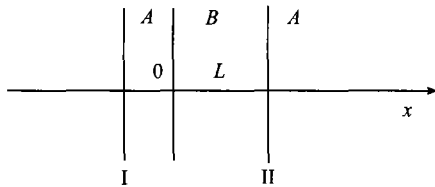


Fig. 2 Diagram of the interface.

Write down approximately the pressure at distance x on the positive side ($x > 0$) as

$$\sigma = \sigma_0 e^{-x/D}, \quad \Delta x = L, \quad (8)$$

where an exponential is used for the approximation of the pressure. This is owing to the fact that the stress depresses the high pressure inside the film at a distance longer than the radius of a dislocation D ^[3], i.e. a gradual decay of this pressure beyond the range D , where the dislocation will break this internal stress.

Now the superposition of the pressures from either side of interface at x is

$$\sigma_s = \sigma_0 \left\{ e^{-\frac{x}{D}} + e^{-\frac{L-x}{D}} \right\}. \quad (9)$$

The total energy inside the sandwich between two neighboring interfaces I and II is expressed as

$$\int_0^L \frac{1}{2\lambda} \sigma_0^2 \left[e^{-\frac{x}{D}} + e^{-\frac{L-x}{D}} \right]^2 dx = \frac{\sigma_0^2}{2\lambda} \left[1 - e^{-\frac{2L}{D}} + \frac{2L}{D} e^{-\frac{L}{D}} \right], \quad (10)$$

where λ is the elastic constant.

4 Optimum energy and size of alternative layers of films

Now we try to find the total optimum energy and optimum size of the eutectic composite system. For simplicity, assume that the stress distribution on the two sides are nearly the same, so only the distribution on one side is to be considered and only half of the energy in Eq. (7) is to be taken into account. Adding the change in free energy (7) and double stress energy (10) together, one has the total change in free energy per unit area of the double charge layer as follows:

$$E = \frac{\sigma_0^2}{\lambda} D \left[1 - e^{-\frac{2L}{D}} + \frac{2L}{D} e^{-\frac{L}{D}} \right] - \frac{1}{2\sqrt{4\pi e^2}} \frac{(B_- - B_+ + \mu)^2}{\sqrt{A_+} + \sqrt{A_-}}. \quad (11)$$

We have a more explicit expression :

$$\varepsilon = \varepsilon(\gamma) \equiv \frac{E}{\frac{\sigma_0^2}{\lambda} L} = \gamma^{-1}(2\gamma e^{-\gamma} - e^{-2\gamma} + \gamma), \quad \gamma = -1 + \frac{\varepsilon_0}{\frac{\sigma_0^2 D}{\lambda}}, \quad \gamma = L/D, \quad (12)$$

where γ represents the breath of sandwich between two successive interfaces, and ε represents the mean energy density inside the sandwich whose optimum value can be obtained by the following condition :

$$\frac{d\varepsilon}{d\gamma} = 0, \quad e^{-2\gamma}(1 + 2\gamma) - 2\gamma^2 e^{-\gamma} + \gamma = 0. \quad (13)$$

Then we have

$$[2\gamma^2 - (1 + 2\gamma)e^{-\gamma}]e^{-\gamma} \equiv f(\gamma). \quad (14)$$

Take $\gamma = 0, 1, 2, 3, 4$, from Eq.(14) we have $f(\gamma) = -1, 0.22, 0.99, 0.89, 0.58$ respectively. From these data and Eq. (12) it follows that γ must lie between 0 and 1. The solution of Eq. (13) is given by the curve $f(\gamma)$ with γ , as shown in Fig. 3. There are two possible solutions: one is a smaller value γ_1 corresponding to the maximum of the energy density, and the other is a larger value γ_2 corresponding to the minimum of the energy density. The former represents stable eutectics, such as Zn-5Al, Fe(γ)-Fe₃C, and the latter represents unstable eutectics.

The case of $\gamma < 0$ and $\gamma > 1$ are not stable. The former represents a state in which the energy ε_0 caused by the differences in chemical potentials of two constituents is too small to overcome that by the lateral pressure due to the difference in electron densities that results in breaking down into macro-size blocks, as in the situation of pure crystals. The latter means that the effect of difference in chemical potentials is so strong that the whole system becomes a mixture, in which small inclusions disperse in main matrix. These inclusions may be metastable solid solution, like phase precipitates Al in CuAl₂, and precipitates in NiC-WC solid solution.^[3] In steel it is Bainits structure.

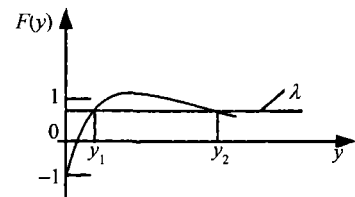


Fig. 3 $f(\gamma) - \gamma$

Let it be noted that in stable eutectic state, the eutectic may still disperse into small inclusions if the matrix is a homogeneous solution.

Hence there are two stable states. One is a eutectic sandwich structure and the other might be an assembly consisting of very fine crystalline mixtures similar to Bainite formed in the later stage of cooling of Austenite after eutectoid, or Leibnite after the eutectic transformation of phases in steel.

The fact that shell structure prevails in water mussels and clams reminds us of the mechanism of the growth of shell structure. The bulk material might grow in alternative shells in eutectic structure.

They first dissolve in the eutectic component and then reconstruct the alternative layers of the eutectic structure.

A study of the mechanism of eutectic structure might be very helpful to designing new materials of very high strength and tenacity, as in shell eutectic structure. The structure of the shells of clams and their fabrication of pearls might give some clue to the solution. Eutectic may coexist in three phases due to crystallines with small interfacial surface tension. If one can find out the prescription to provide eutectic material, the growth and reconstruction of the bulk of shelling materials would be readily brought to light.

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